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Determination of iron in seawater: From the laboratory to *in situ* measurements

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ABSTRACT

The marine biogeochemistry of iron plays a significant role in regulating climate change. Trace dissolved iron in oceanic surface water can limit phytoplankton growth which in turn limits the carbon dioxide flux at the air/sea interface. To better understand the relationship between iron and its different species with phytoplankton, as well as the biogeochemical cycle of iron in seawater, accurate, sensitive, and *in situ* methods are needed for iron determination. This paper reviews the methods for determining iron in seawater from the laboratory, shipboard to *in situ* measurements, including such strategies as atomic spectrometry, spectrophotometry, chemiluminescence, and voltammetry, which will provide the foundation for developing reliable long-term iron monitoring and sensing platforms in the future.

1. Introduction

Iron is one of the most abundant elements in the earth's crust (5%) [1]. However, its concentration in seawater is extremely low (0.1–10 nmol L^{-1}) [2]. Iron is biogenic and plays an important role in photosynthesis because it exists at the active sites of molecules which are responsible for oxygen transport and mitochondrial electron transfer [3], making it an essential trace element for phytoplankton growth in marine ecosystems. Iron bioavailability is thought to be a limiting factor for primary productivity in approximately 40% of the world's oceans [4], including the subarctic Pacific, the equatorial Pacific, and the Southern Ocean, which are all known as high-nutrient, low-chlorophyll (HNLC) oceanic regions. Even in coastal environments where the total iron concentration is much higher, iron bioavailability is still quite low [5]. If concentrations exceed physical requirements, Fe may become toxic, acting as an enzyme inhibitor [6] and, moreover, causing oxidative injuries and abnormalities in Fe metabolism, of which the effects may further extend to other biological activities such as behavior, growth, and reproduction [7]. The marine biogeochemistry of iron is highly influenced by its low solubility, redox speciation, and its role in biological cycles [8].

Different species of iron are known to exist in seawater. Historically, different forms of iron were defined as that which passes through a 0.45, 0.4 or 0.2 μm filter membrane. With the development of ultrafiltration technique, the physical-chemical forms of iron are defined as particulate iron (> 0.20 μm), colloidal iron (0.02–0.20 μm), and dissolved iron (< 0.02 μm) in seawater nowadays [9]. They are dependent on the equilibrium between various particulate and dissolved phases, and the transformation model between the physical-chemical species is shown in Fig. 1. Iron exists in four different states, such as 0, +II, +III and +VI. The most common species fall under oxidation states +II and +III which can form salts with common anions. Dissolved Fe(II) and Fe(III) are believed to be available to biota, while there is no uptake of colloidal or particulate iron in the absence of thermochemical or photochemical dissolution [10,11]. This means that increasing the solubility of iron in seawater is likely to increase its bioavailability. The redox transition between oxidation states +II and +III is dependent on pH and electron activity (pE) [12]. The solubility of Fe(III) hydroxide in seawater (25 °C, pH 8.1, 0.7 mol L^{-1} NaCl) has been reported to be ~ 10^{-11} mol L^{-1} [13] while the solubility of Fe(II) is much higher than Fe(III) with respect to thermodynamic properties. However, Fe(II) is easily oxidized to insoluble Fe(III) in oxygen-rich environments [14]. Due to the existence of natural organic Fe chelators in seawater, it is thought that up to 99% of dissolved iron has complexed with iron-binding ligands [15], indicating that iron redox in seawater is strongly dependent on the concentration and properties of

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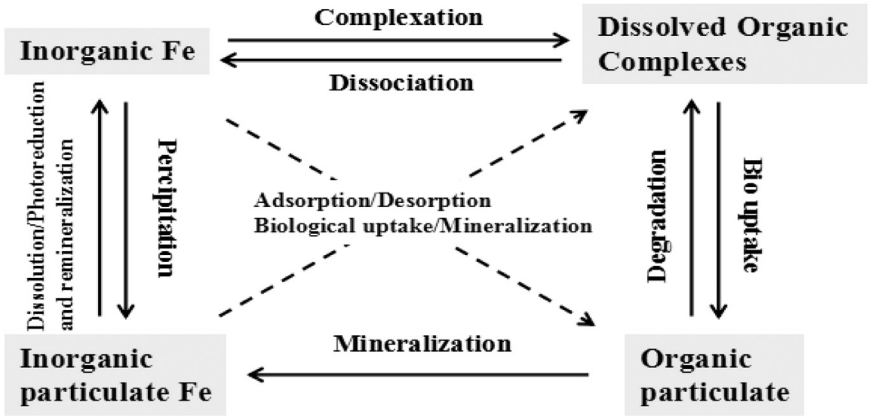

Fig. 1. A diagram of iron phase transfers and related processes in seawater (Reprinted with permission from [10] Copyright © Elsevier).

these ligands. Strong complexes formed with organic compounds potentially maintain enhanced dissolved Fe concentrations [16] and may permit dissolved Fe concentrations to exceed the solubility product of dissolved inorganic Fe in seawater [17]. In addition, Fe solubility may increase with decreasing temperature, decreasing pH, and decreasing salinity [18]. Thus the concentration of dissolved iron and its different species in seawater play an important role in the growth of marine organisms, influencing the global carbon cycle and consequently global climate change [19]. Hence it is important to understand the marine biogeochemistry of iron, through the accurate determination of trace iron and its speciation in seawater. However, the onboard determination of trace iron, especially its different species in the open ocean, is one of the most challenging problems in marine environment analysis [20].

Determination of iron in seawater has attracted more and more attention recently. In 2014, Worsfold et al. dedicated a review to introduce suitable analytical approaches for determination of dissolved iron in seawater [8], which mainly focused on the processes from sampling and sample treatment, detection methods to quality assurance of the data. In this review, the evolution of the detection method of iron in seawater from the laboratory, shipboard to *in situ* measurements has been overviewed. Meanwhile, the trends, new detection schemes, features and drawbacks of different analytical methods have been proposed and discussed.

2. Sampling and sample treatment

The acquisition and storage of clean and stable samples are key measures that ensure data quality for iron concentrations in seawater. Therefore, there is a need to have a standard protocol. Section 6 of the GEOTRACE program guide [21] contains sampling and handling protocols for trace metals (including iron). In the ocean, preventing sample contamination is the utmost priority. The most commonly used clean sampling systems for vertical profiling are commercial PTFE-lined Go-Flo or Niskin samplers with PTFE coated rosette-based systems [22]. Sample handling, reagent preparation, and iron analysis must be conducted under a laminar-flow clean hood with filtered air [23]. Sample storage requires ultra-clean containers. Low-density polyethylene (LDPE) and high-density polyethylene (HPDE) bottles are recommended for trace iron determination [21]. These containers must be thoroughly cleaned using an acidic solution according to the recommended protocols [21].

For samples used for total dissolved iron content, the samples need to be acidified to pH < 2.0 using a guaranteed pure HCl or HNO_3 solution that has been re-distilled on a cold finger silica distillation apparatus or Teflon stills [23]. To analyze the different species of iron, reagents used to determine their distribution [24,25] or the direct determination of Fe(II) should be carried out immediately after sampling and measured onboard the ship due to the high reactivity of certain iron species, especially Fe(II).

3. Laboratory methods

3.1. Atomic spectrometry

The most common method used to determine iron in seawater requires pre-concentration coupled with atomic spectrometry, such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and so on. The most popular solvent extraction method was reported by Bruland et al. [26] in 1979 with a double extraction into chloroform after chelating with ammonium 1-pyrrolidinedithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC), then back-extraction into nitric acid. A detection limit of 50 pmol. L^{-1} for graphite furnace atomic absorption spectrometry (GFAAS) using the above solvent extraction pre-concentration was reported by Landing and Bruland in 1987 [27]. On-line solid phase pre-concentration gained increasing attention in the late 1980s [28] after a detection limit of 150 pmol L^{-1} was reported by Saager et al. [29], based on a Chelex-100 column for GFAAS. However, these methods usually required samples greater than 250 mL and determination was limited by high reagent blank concentrations and contamination [26].

Thus, how to improve the detection limit and decrease the volume of sample used have been the main direction for research in determining iron in seawater by atomic spectroscopy. High resolution (magnetic sector) ICP-MS with high sensitivity and a short detection time has recently become widely used to lower the detection limit and improve the detection sensitivity [30–32]. Isotope dilution is now frequently used for quantification because it does not require standard addition or external standards that can greatly minimize the deviation due to matrix interference and recovery variations [8]. The co-precipitation pre-concentration methods required minimal use of reagents, which therefore can significantly lower the reagent blanks [32]. The task-specific ionic liquid (TSIL) of 1-ethyl-3-methylimidazolium bromide functionalized with 8-hydroxyquinoline was used as a chelating agent and extracting solvent for dispersive liquid–liquid micro-extraction offers advantages such as simplicity, ease of operation [33]. Based on the above advantages, the lowest detection limit for atomic spectrometry is 2 pmol L^{-1} using a magnesium hydroxide co-precipitation method with a high resolution ICP-MS reported by Wu [34], or 14 pmol L^{-1} by using a Nobias Chelate PA1 resin that has been co-immobilized with ethylenediaminetriacetic acid and iminodiacetic acid on a high resolution ICP-MS reported by Biller and Bruland [30]. The minimum required sample volume was 12 mL using isotope dilution with a high resolution ICP-MS method, reported by Milne et al. [31]. A novel automated off-line preconcentration system for trace metals (Al,

Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in seawater was developed through improving a commercially available solid-phase extraction system SPE-100 (Hiranuma Sangyo). The nine trace metals were simultaneously and quantitatively pre-concentrated from 120 g of seawater by the single-step preconcentration combined with high-resolution ICP-MS [35]. Significant improvements have been made in the determination of iron in seawater using atomic spectrometry, but cumbersome equipment and complex pre-treatment as well as expensive costs for testing restrict its application *in situ* use at sea. This is more commonly an analysis reserved for laboratories on land in a controlled environment. Additionally, atomic spectrometry can only determine the total dissolved iron.

3.2. Spectrophotometry

Spectrophotometric techniques involve ligands that can selectively combine with iron (a particular redox state) to form a colored complex with high molar absorptivity. The initial ligands that were used for iron determination were 2,2′,2″-tripyridyl [36], 2,2′-bipyridyl [37], and thiocyanate [38]. Total dissolved iron was determined after the reduction of Fe(III) and these ligands were used to bind Fe(II). Later, more selective and sensitive ligands for iron complex, such as 1,10-phenanthroline [39], 2,4,6-tripyridyl-1,3,5-triazine [40], and bathophenanthroline [41], were used for iron spectrophotometric determination. Although the spectrophotometric method has the advantage of being an inexpensive and simple procedure, its sensitivity does not meet the requirements for determining trace iron in seawater directly. Thus, more selective and sensitive ligands have been developed to meet the required limits of detection. A chelating resin is definitely needed for Fe determination. One reason is to pre-concentrate iron while another is to separate it from the bulk seawater matrix. The most widely used functional chelating group is 8-Hydroxyquinoline (8-HQ), which is immobilized on a vinyl polymer resin. Many chelating resins, such as Toyopearl TSK [42], Toyopearl AF-Chelate-650 [43], and NTA "Superflow" [44], are commercially available. Ferrozine (3-(2-bipyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine) has been widely used in Fe(II) determination because it can form a colored stable Fe(II)-ferrozine complex with high molar absorptivity ($\lambda = 562$ nm) [45]. Blain and Treguer [46] used ascorbic acid to reduce Fe(III) to Fe(II) and calculated the total dissolved iron. Using this on-site reduction system, one can obtain the redox speciation of Fe(III), Fe(II), and total dissolved iron. The drawback of the spectrophotometric method is that the complexing ligand (such as ferrozine) may change the iron redox speciation under certain conditions [47]. Another thing to point out is that pH is an important parameter for the recovery of Fe(III) and Fe(II) from the pre-concentration column. Obata et al. [48] reported that Fe(III) can be collected from 8-HQ at pH 3.0–4.2 while Fe(III) and Fe(II) can be recovered at pH 5.2–6.0. In ferrozine methods, sample acidification can also promote the reduction of Fe(III) to Fe(II), which will change the redox speciation. For these reasons, how to quickly determine transient Fe(II) in un-acidified samples for iron redox analysis is still a challenge.

Except for the ferrozine method, the catalytic oxidation of DPD (N,N-dimethyl-p-phenylenediamine dihydrochloride) by Fe(III) in the presence of H_2O_2 [49,50] is also a widely used spectrophotometry method for iron determination. DPD can be oxidized by Fe(III) and H_2O_2 is introduced to ensure all iron in the solution has been transformed into Fe(III). The amount of oxidized DPD can be detected spectrophotometrically ($\lambda = 514$ nm) [51] and it is proportional to the concentration of iron. The disadvantage of catalytic DPD method is that it cannot determine redox iron speciation.

3.3. Chemiluminescence

The most popular chemiluminescence (CL) reaction, luminol (5-amino-2,3-dihydro-1,4-phthalazinedione)-H_2O_2, has been widely applied in the detection of various substances [52]. O'Sullivan et al. [53] and King et al. [54] adapted the chemiluminescence technique for use in seawater and luminol-CL reactions have been used for trace iron determination in seawater based on the catalytic effect of either Fe(III) or Fe(II) on the oxidation of luminol to generate blue luminescence ($\lambda \sim 440$ nm). In addition to luminol, brilliant sulfoflavin (4-amino-*N*-*p*-tolyl)-naphthalimide-3-sulfonate was also used for Fe(II) and total dissolved iron determination in seawater [55,56]. Prior to determining the total dissolved iron, a reducing agent (eg. ascorbic acid) was needed to reduce Fe(III) to Fe(II).

Chemiluminescence is often used along with flow injection analysis (FIA) technology in the determination of iron. For laboratory experiment, the main purpose of using chemiluminescence method is to constrain iron concentrations within seawater kinetic models. Rose and Waite [57] used luminol-CL method to measure Fe(II) and developed a detailed kinetic model to understand the oxidation process of Fe(II) in seawater in the absence and presence of natural organic matter. Results showed that the presence of a relatively strong Fe(III) binding ligand significantly increased the rate of Fe(II) oxidation, while ultimately retaining most of the iron in the system in dissolved form.

3.4. Voltammetry

Accurate determination and quantification is required for trace iron and its species in seawater. Compared to other analytical methods, such as spectrometry [26,27,30,31], spectrophotometry [45,46,48], and chemiluminescence [58], voltammetry has the advantage of being low cost, simple, fast, highly sensitive, and it can determine trace iron and iron species in seawater. The low solubility of iron in mercury [59] and the direct reduction of Fe(III) to element metal coincides with the hydrogen reduction in an acidic solution [60]. This limits the voltammetric stripping of iron *via* metal and also means that iron can't be quantified using conventional anodic stripping voltammetry. Thus, the electrochemical methods used to determine iron content can be divided into two groups: one is based on the direct reduction reaction of Fe(III) to Fe(II) on the working electrode, and the other is based on adsorptive cathodic stripping voltammetry, in which an iron-binding ligand is added to form a complex with Fe(III) and analysis is performed on the cathodic stripping of the Fe(III)-complex. Competitive ligand adsorptive cathodic stripping voltammetry can also be used to analyze different species of iron.

A key issue in the quantitative analysis of iron based on the direct reduction of Fe(III) is how to improve the sensitivity, stability, and anti-interference ability of the working electrode. Štulíková and Vydra [59] used a rotating carbon disk electrode to cathodically detect Fe(III) with a detection limit of 0.1 μmol. L^{-1} in acidic media after deaeration. But the detection limit was too high for trace iron determination in seawater, indicating that the working electrode needed to be modified. Pan's group recently have developed a series of modified electrodes to sensitively and selectively detect total dissolved iron in coastal waters without using complexing ligands [61–65]. For example, Lin et al. [64] used a nanocomposite of reduced graphene oxide/methylene blue/gold nanoparticles to modify GCE and the sensitive cathodic signal of Fe(III) was achieved with a detection limit of 15 nmol L^{-1} in 0.1 M HCl without requiring the use of complexing ligands for Fe(III). Li et al. [63] reported a sensitive determination of Fe(III) in coastal waters based on ionic liquid-reduced graphene oxide-supported gold nanodendrites with a detection limit of 35 nmol L^{-1}. Han et al. [61] achieved a controlled synthesis of dendritic gold nanostructures using graphene oxide on GCE and a morphology-dependent performance for Fe(III) determination with a detection limit of 15 nmol L^{-1}. Lin et al. [65] took advantage of the synergistic effects between titanium carbide nanoparticles and Nafion to modify GCE and the catalytic amplifying effect of oxidant hydrogen peroxide, achieving a detection limit of 7.2 nmol L^{-1} for Fe (III). Hu et al. [62] used a graphene oxide-assisted synthesis of bismuth nanosheets, modified GCE, and oxidant $KBrO_3$ to catalytically detect Fe (III) at a limit of 2.3 nmol L^{-1}. To date, the determination of iron based

on the direct reduction of Fe(III) without any complexing ligands has been widely used in laboratory measurements for total dissolved iron because it is easy, cheap and sensitive.

The electrochemical determination of total dissolved iron based on direct measurement of Fe(III) has the advantage of being inexpensive, simple, fast, and sensitive, but the detection limitations cannot meet some of the requirements of trace iron in seawater and may be complicated by interference in seawater samples. Adsorptive cathodic stripping voltammetry based on the signal of iron-binding ligands provides a good solution to this problem. The chelating reagents include catechol [66], salicylaldoxime [67], 1-nitroso-2-napthol [68], 2-(2-thiazolylazo)-p-cresol [69], and 2,3-dihydroxynaphthalene [20,23,70]. In addition, the sensitivity can be catalytically increased by adding oxidizing agents, such as H_2O_2, $KBrO_3$, ClO_2^- [25,68]. The most sensitive method for iron determination in seawater was reported by Laglera using 2,3-dihydroxynaphthalene as the complexing ligand and $KBrO_3$ as the oxidizing agents, with a detection limit of 5 pmol L^{-1} for Fe(III) [20]. The ligands mentioned above typically use a mercury electrode as the working electrode. Mercury electrodes are well known for their toxicity and the inconvenience associated with handling them [71], which restrict their wider use, especially onboard determination. Bismuth is the most popular alternative mercury-free electrode material and has been widely used in the determination of iron with help of complexing ligands. Segura et al. [72] used 1-(2-piridylazo)-2-naphthol (PAN) as the complexing ligand for Fe(III), and Fe(III)-PAN was adsorbed onto a bismuth-coated GCE with a 60 s adsorption time followed by square wave cathodic stripping voltammetry to obtain a detection limit of 1.79 nmol L^{-1}. Lin et al. [73] introduced a new environmentally-friendly electrode called a tin-bismuth alloy electrode to solve some of the differences in determination due to the inhomogeneous bismuth film and the plating potential and substrate electrode depended morphology. They also chose PAN as the Fe(III) complexing ligand and obtained a detection limit of 0.2 nmol L^{-1} using differential pulse adsorptive stripping voltammetry with an adsorption time of 60 s. Bobrowski et al. [74] used triethanolamine (TEA) as the Fe(III) complexing ligand and $KBrO_3$ to rapidly oxidize Fe(II)-TEA to Fe(III)-TEA, therefore achieving a detection limit of 7.7 nmol L^{-1} on a bismuth film electrode in alkaline solution. Zhu et al. [75] utilized a GCE modified with reduced graphene oxide and gold nanoparticles and the complexing ligand 2-(5-bromo-2-pyridylazo)=5-diethylaminophenol (5-Br-PADAP) to detect total dissolved iron in coastal waters, reporting a detection limit of 3.5 nmol L^{-1}. Lin et al. [76] used 2,2′-bipyridyl as the complexing ligand for Fe(II) and achieved a sensitive determination for Fe(II) in coastal waters based on titanium carbide nanoparticles/Nafion/platinum nanoflowers modified GCE with the lowest detectable concentration of 0.1 nmol L^{-1}.

Another significant advantage of the electrochemical method compared to other analytical methods for iron determination in seawater is that it can be used to determine iron speciation. It is very important to determine the iron species because iron is thought to be a limiting nutrient for phytoplankton growth, while Fe(II) might be a preferred nutrient [77]. The biological role of iron-binding ligands and the rate at which organically bound iron becomes bioavailable require more investigation because some ligands, like siderophores and porphyrins, may be selectively released by organisms and can organically complex with dissolved iron [78]. Additionally, little is known about the speciation of Fe(II) in seawater and the extent to which Fe(II) is organically complexed. Understanding the different species of iron found in seawater is needed to better understand the effect of organic complexation on iron bioavailability and the biogeochemical cycling of iron. To obtain the concentration of labile iron, voltammetric determination was used to compare the natural and added ligands using cathodic stripping voltammetry [67,68]. The equation can be described as $[Fe^{3+}]/[Fel] = [Fe^{3+}]/C_L + 1/(K_{Fel}C_L)$, where [FeL] is the concentration of iron complexed with the natural ligand L, C_L is the total concentration of L, and K_{FeL}' is the conditional stability constant of [FeL] [68]. This titration experiment can be carried out onboard and has been widely applied in onboard measurements of trace iron and iron speciation [23,70].

4. Shipboard methods

Requirements for portable methods that are suitable for onboard use at sea are intended to simplify sample pre-treatment and minimize sample storage. FIA has the advantage of easy automatic operation and high sample throughput, which provides an excellent platform for sample handling [79]. Recently, FIA has been widely used for shipboard measurements of iron in conjunction with other detection methods, especially for iron redox speciation analysis because it can greatly minimize the redox change and contamination. The primary detection methods are spectrophotometry (SP) and chemiluminescence (CL) and voltammetric method. Typical flow injection manifolds for the determination of iron based on FIA-SP and FIA-CL [80] are shown in Fig. 2.

4.1. Flow injection with spectrophotometry

FIA using on-line pre-concentration provides an excellent platform for sample handing. One reason is to pre-concentrate iron while another is to separate it from the bulk seawater matrix. King et al. [81] used a C_{18} column with ferrozine to pre-concentrate Fe(II), then spectrophotometrically detected the iron concentration in the solution to elute the complex from the C_{18} column. Later, O'Sullivan et al. [82] added an *in situ* sampling system to the detection system described above for on-site determination. They studied the Fe(II) distribution in the equatorial Pacific and found that concentrations varied from 120 to 500 pmol L^{-1}. Measures et al. [49] reported a detection limit of 25 pmol. L^{-1} using FIA equipped with an 8-HQ micro-column. Lohan et al. [50] reported a detection limit of 24 ± 4.9 pmol L^{-1} (n = 9) for Fe based on the FIA-DPD method. For seawater samples collected in the North Pacific Ocean, the average concentration of total dissolved iron in the surface samples was 0.101 ± 0.009 nmol L^{-1} (n = 14) and in samples from 1000 m in depth was 0.93 ± 0.04 nmol L^{-1} (n = 18).

Recently, another spectrophotometrical technique that uses a long path length liquid wave guide capillary cell (LWCC) has been widely used to lower the detection limit of iron. The detection mechanism is same as the spectrophotometric methods described above. Zhang et al. [83] used a ferrozine method combined with a 2 m LWCC for iron speciation in seawater with a detection limit of 0.1 nmol L^{-1}. Huang et al. [84] used ferrozine as the complexing ligand and LWCC as the detection technique to carry out real time redox speciation (Fe(II), Fe(III), Fe(II + III)) of iron in the surface waters of the East China Sea. The biggest advance was that they updated the single carrier stream design (as shown in Fig. 2a) to dual carrier streams to minimize the Schlieren effect caused by the variation in salinity (as shown in Fig. 3).

In addition to normal FIA (nFIA), a reverse FIA (rFIA) method reported by Huang et al. [85] has been used to determine the total dissolved iron in estuarine and coastal waters collected from the Pearl River Estuary based on DPD methods. The detection limit was 0.4 nmol L^{-1}, which was lower than half of that of the nFIA method. Fig. 4 shows the manifold of this rFIA system. The difference between nFIA and rFIA is that rFIA uses samples as the carrier and the reagents are injected into the carrier, which is opposite of the nFIA procedure [85]. rFIA consumed less reagents and the sample throughput of rFIA (10 h^{-1}) was much higher than in the nFIA (4 h^{-1}) method, so rFIA is believed to be more suitable for long-term shipboard use.

4.2. Flow injection with chemiluminescence

FIA-CL is a sensitive method that has been developed to determine iron in seawater. Careful adjustment of the pH and an on-line pre-concentration with 8-HQ [25,86] to remove matrix and pre-concentrate

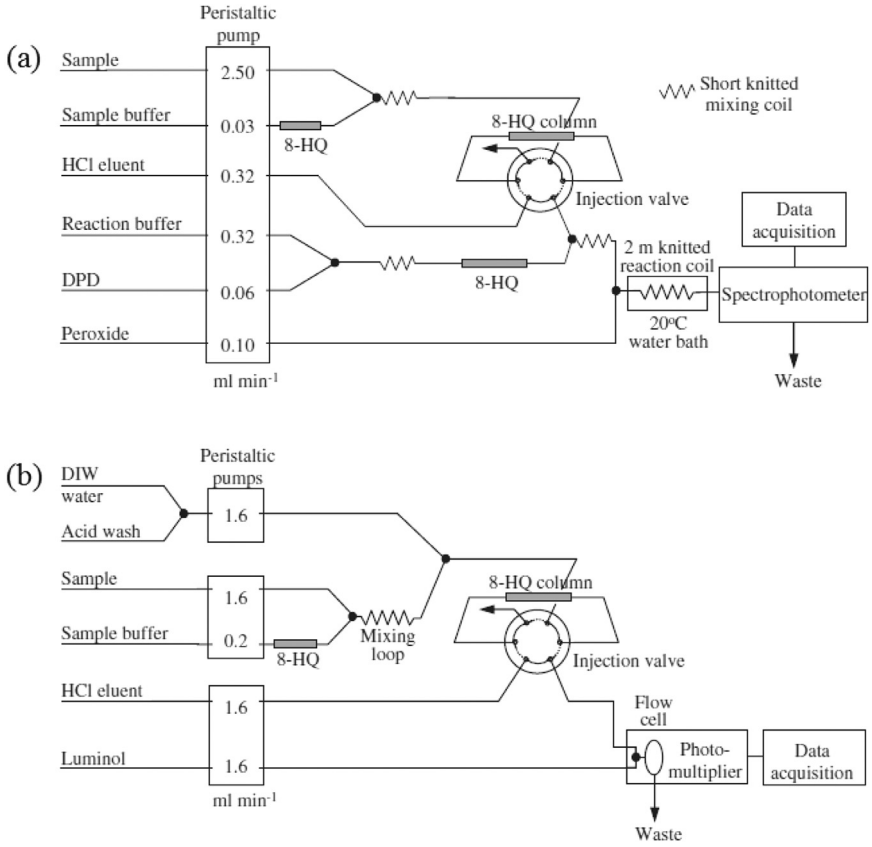

Fig. 2. The typical flow injection manifolds for iron determination based on (a) FLA-SP and (b) FLA-CL (Reprinted with permission from [80] Copyright © John Wiley and Sons).

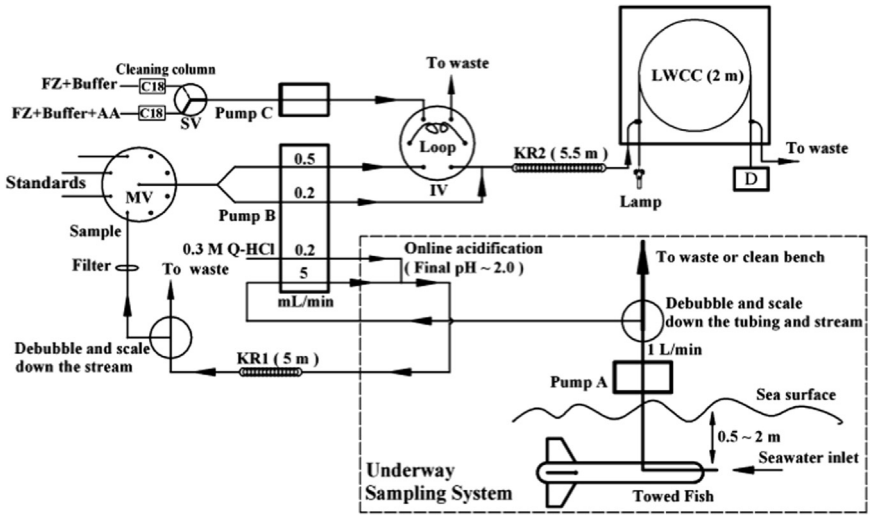

Fig. 3. The manifold configuration of real-time iron speciation system based on Fe(II)-ferrozine and LWCC (Reprinted with permission from [84] Copyright © American Chemical Society).

iron are needed to achieve the highest sensitivity and avoid precipitation [87]. Bowie et al. [58] reported a sensitive onboard determination system for Fe(II) and total dissolved iron based on a FIA-luminol-CL method with a detection limit of 40 pmol L^{-1} (3 s). As shown in Fig. 5, an off-line reduction of Fe(III) to Fe(II) in acidified samples was conducted first, followed by an in-line matrix elimination and pre-concentration on an 8-HQ column under pH 5.0 as well as merging with a luminol/carbonate buffer reagent stream to detect the total dissolved iron after eluting Fe(II) from the resin using HCl.

The manifold for Fe(III) and total dissolved iron determination based on the FIA-luminol-H_2O_2-CL method is shown in Fig. 6 [48]. Acidified samples are firstly oxidized from Fe(II) to Fe(III) off-line by H_2O_2, then buffered to a pH of 3.0 in-line prior to pre-concentration. After eluting Fe(III) from the resin using HCl, streams of luminol/carbonate and Fe(III) with H_2O_2 are mixed for detection by a photomultiplier tube [88]. Klunder et al. [88] used the FIA-luminol-H_2O_2-CL method with pre-concentration on an iminodiacetic acid (IDA) resin to detect Fe(III). The detection limit of this method was

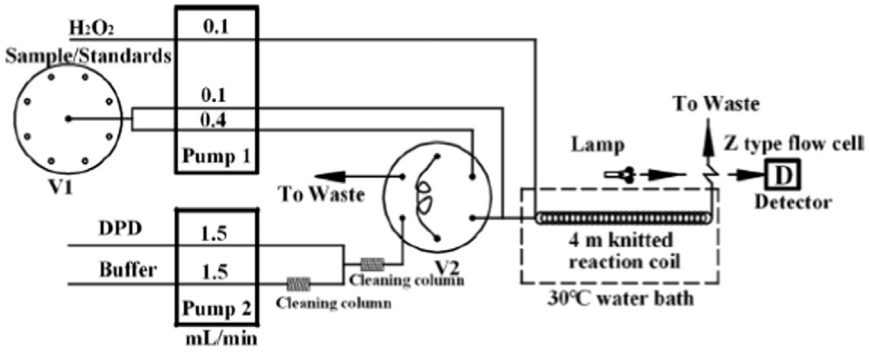

Fig. 4. The manifold configuration of rFIA based on DPD and the H_2O_2 method (Reprinted with permission from [85] Copyright © Elsevier).

5.7 ± 2.9 pmol L^{-1} and it has been applied for shipboard use to accurately determine the distribution of dissolved iron in the southern Atlantic Ocean. Cannizzaro et al. [89] determined the total dissolved iron in Tamar Estuary (UK) with a detection limit of 40 pmol L^{-1} (3 s) using a luminol reaction with dissolved oxygen as the oxidant to replace H_2O_2 based on flow injection. Oliveira et al. (2015) developed a preliminary protocol for Fe(II) determination in acidified seawater based on the reaction between Fe(II) and luminol. They proposed a novel micro-sequential injection (μSI) fluidic protocol and two distinct strategies for photon collection, that was the first application of chemiluminescence detection under lab-on-valve (LOV) format [90]. The long-term stability of luminol solution and its low consumption per determination (100 μL), combined with the rapid analytical throughput (116 determinations per hour), make this approach well suited to shipboard analysis of Fe(II) with potential for autonomous operations.

4.3. Flow injection with voltammetry

Voltammetry has recently been found to be useful in the on-site determination of trace metals [91–94]. It does not require a matrix removal step and can be used for the determination of a wide range of metals, which can greatly simplify the procedure and minimize the contamination and redox change in pre-treatment [95] to improve iron determination *in situ*. Fig. 7 shows the manifold of an automated voltammetric system that has already been used for shipboard analysis of trace metals. Achterberg and van den Berg [91] applied this in-line automated voltammetric system to determine the total dissolved Cu and Ni in the North Atlantic and Western Mediterranean. They later [92] introduced complexing ligand titrations to this system and were able to automatically record reliable copper concentrations (in the Atlantic Ocean) and redox chromium types (in the Mediterranean) based on the differentiate between Cr(III) and Cr(VI) using onboard adsorption of Cr (III) on silica particles. The working electrode used in this system was a hanging mercury electrode [91,92]. Mikkelsen et al. introduced an automatic monitoring system for the continuous monitoring of Zn and Fe in river water, drainage water, and waste water at low concentrations [96]. The manifold of this system is shown in Fig. 8. The working electrode that used was a dental amalgam electrode (DAM, $d \approx 2.5$ mm), an environmentally-friendly alternative to the liquid mercury electrode in the field. The detection strategy was based on the re-oxidation of iron deposited on a solid amalgam electrode surface and had a stripping peak of iron at around − 0.65 V. The frequency of maintenance required for this system varied from once a week in wastewater to once a month in river water. Those automated voltammetric determination of trace metals discussed above can provide feasible solutions to realize the *in situ* analysis of iron in seawater. Additionally, the Au-Hg microelectrode has also been used for *in situ* measurements of Fe [97,98]. It has been used to detect Fe(II) with a detection limit of 25 μmol L^{-1} in seawater [97] and 10 μmol L^{-1} in freshwater due to the elimination of sodium interference [98].

4.4. Flow injection with other methods

Multisyringe flow injection analysis (MSFIA) was established combining the advantages of several techniques: working in parallel like FIA, robust like sequential injection analysis (SIA), and using solenoid valves like multi-commutation flow injection analysis (MCFIA) [99]. Few works have been established by coupling of MSFIA systems with atomic absorption spectrometry (AAS). MSFIA systems coupled with hydride generation atomic fluorescence spectrometry (HG-AFS) have been often employed for the determination and speciation analysis of elements [35,99,100]. A 3D printed device with a disk-based solid-phase extraction for the automated speciation of iron using the multisyringe flow injection analysis technique has been reported by Calderilla et al. [101]. Using 3D printing techniques has the advantages of being simple, fast and low-cost. Thus, it is highly desirable for the development of novel devices. In addition, integrated 3D printed devices are a step forward toward the full reproducibility of complex flow-based networks for automated *in situ* chemical analysis.

5. *In situ* methods

Carrying out the *in situ* analysis of iron speciation is an important component of research on the iron biogeochemical cycle. However, ICP-MS and AAS have a limited range for use and are not suitable for on-site measurement. Colorimetry and chemiluminescence combined with FIA have a lower detection limit for iron and can determine redox iron species, but they require complicated pre-concentration procedures and matrix removal. Voltammetric techniques are very suitable to design probes for trace metal analysis and can analyze a large number of trace compounds at low detection limit, while also measuring different iron species based on the redox state and liability of metal species [102].

However, many applications were limited to short-term *in situ* analysis in surface waters. Long-term voltammetric monitoring at different depths faces challenges such as insufficient reliability of sensors, fouling of the sensor surface, interferences from dissolved oxygen and pressure, and more [102]. The Voltammetric *In Situ* Profiling System (VIP system) firstly developed by Tercier et al. [103] provides a solution to the above problems and has now been commercialized for continuous *in situ* analysis of trace metals [94,103,104]. The manifold of the VIP system is shown in Fig. 9(A). The VIP system contains a submersible voltammetric probe, a multi-parameter probe (including temperature, salinity, pressure, conductivity, O_2, and pH), an on-line O_2 removal module, and a telemetry unit connected to a laptop computer, and it can also be controlled onboard or automatically following pre-programmed instructions. The electrochemical measurements are conducted within a mini-voltammetric cell (internal volume of 1.5 mL) and the gel-integrated microelectrode (GIME) is used as the working electrode. The GIME is a Hg-plated-Ir microelectrode covered by an agarose gel that functions as a small separation/reaction chamber with fast diffusion transport and also protects the surface from fouling [103]. The

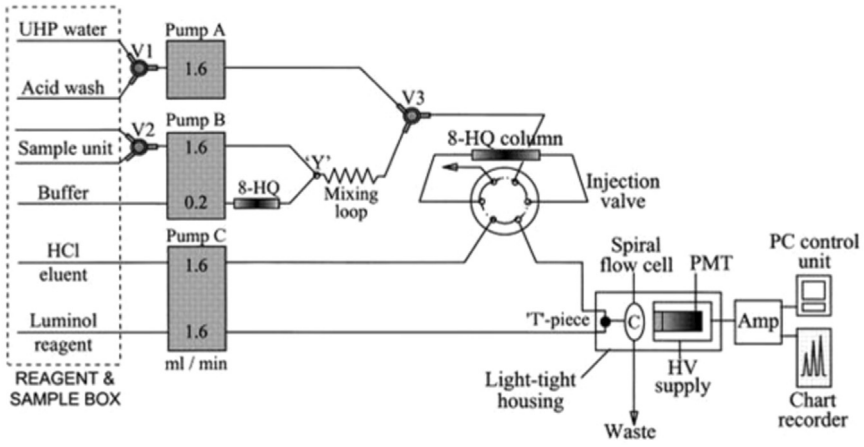

Fig. 5. The manifold for determination of Fe(II) and total dissolved iron based on the FIA-luminol-CL method (Reprinted with permission from [58] Copyright © Elsevier).

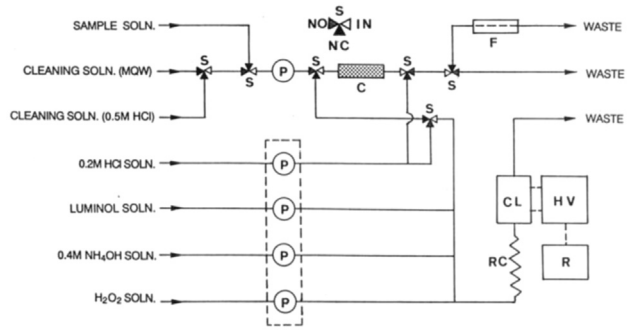

Fig. 6. The manifold for Fe(III) and total dissolved iron determination based on the FIA-luminol-H_2O_2-CL method (Reprinted with permission from [48] Copyright © American Chemical Society).

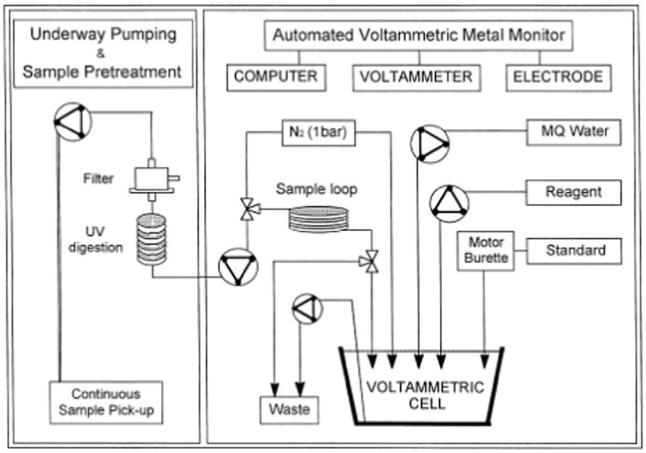

Fig. 7. The manifold of an automated voltammetric system for shipboard analysis of trace metals (Reprinted with permission from [91,92,95] Copyright © Elsevier).

voltammetric analysis is performed after a 5–10 min' equilibration period in the agarose gel (typically for a membrane of 300 μm) with the solution [102]. The detection limits for square wave cathodic stripping voltammetry measurements of Fe(II) and Mn(II) based on the interconnected GIME were 1 μmol L^{-1} and 0.1 μmol L^{-1}, respectively [104]. The GIME can also be modified with a thin layer (a few μm) of a complexing resin called CGIME [105] to achieve sub-nanomolar detection of free metal-ions in complicated systems. Different from measurements using GIME, an additional step is needed to release the trace

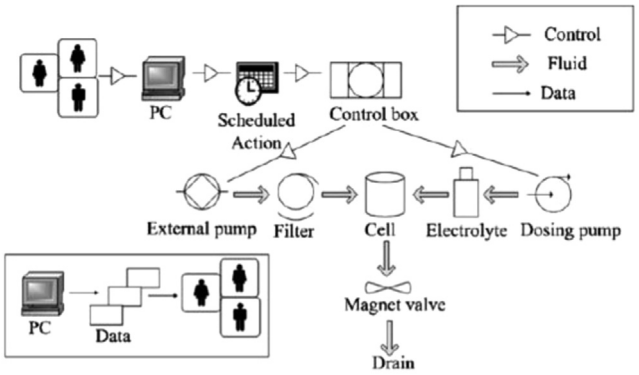

Fig. 8. The manifold of Mikkelsen et al.'s reported automatic monitoring system for continuous monitoring of Zn and Iron concentrations (Reprinted with permission from [96] Copyright © John Wiley and Sons).

metal accumulated in the sample during the resin equilibration, prior to voltammetric analysis [102]. Detection limits for Cu(II), Pb(II), and Cd (II) are 20, 10, and 60 pmol L^{-1}, respectively, with an accumulation time of 1 h using square wave anodic stripping voltammetry based on CGIME [105].

More recently, an improved VIP called the Multi Physical Chemical Profiler (MPCP) has been developed for *in situ* monitoring of trace metal species in various estuaries and coastal seawaters [106]. The manifold of MCPC is shown in Fig. 9(B). Compared to the VIP system, MCPC consists of three different flow-through cells with their own fluidic systems. One cell is equipped with CGIME and another two cells are equipped with GIME. CGIME is used to obtain the concentration of free metal ions. One GIME in channel 1 is used to measure the concentration of dynamic metal species. The GIME coupled with a FIA for automatic on-line sample pretreatment in channel 3 is used to obtain the total extractable metal concentration by complexing with strong triethyleneteramine followed by acidification and heating. Subtracting the dynamic metal species from the total extractable metal concentration reveals the concentration of metal bound to particles and colloids [102,106]. MCPC has been successfully used in Cu and Pb speciation analysis in the Po estuary of the Adriatic Sea [106]. VIP and MCPC have been shown to provide reliable, real-time monitoring of metals and their species with less than 10% variations over a continuous field survey for up to 8 days without renewal of the sensor [104,106], and they provide an exciting new platform for real-time monitoring of trace Fe and its species in seawater in the near future.

Aside from the *in situ* sensors described above which are mostly used for trace metal analysis, there have latest developments in *in situ* sensors

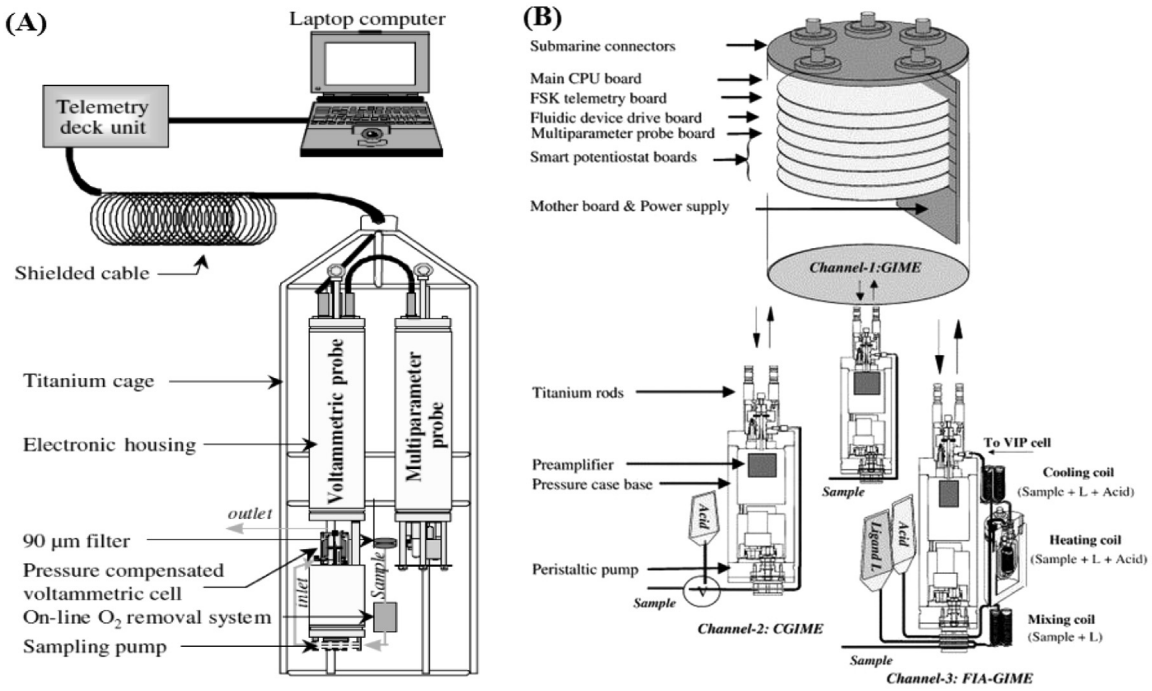

Fig. 9. (A) The manifold of a VIP system (Reprinted with permission from [103] Copyright © John Wiley and Sons), and (B) a MCPC system (Reprinted with permission from [106] Copyright © Elsevier).

based on new strategies for Fe determination in seawater for low cost and reliable long-term monitoring. Chung Chun Lam et al. [107] described an optical sensor in 2006 that overcome the issues of the matrix interference with seawater, biofouling, and long-term stability, *etc*. They achieved a detection limit of 40 pmol L^{-1} for the direct measurement of Fe(III) with a working range of 50–1000 pmol L^{-1} using a fluorescence quenching-based siderophore (parabactin) biosensor. Additionally, this *in situ* sensor had a reproducibility of 6% (n = 10) for 1000 pmol L^{-1} Fe(III). Roy et al. [108] designed a device that includes an iron-specific chelating biomolecule, desferrioxamine B (DFB), which is covalently immobilized on a mesoporous silica film. The device can provide an accurate and precise measurement of iron according to the infrared spectral changes of immobilized DFB upon Fe(III) complexation on the surface of a chip exposed to seawater. The detection limit of this device is about 50 pmol L^{-1} for samples acidified to pH 1.7. This device has been successfully applied for *in situ* measurement of dissolved iron in subarctic Pacific seawater and can be deployed on an autonomous platform for long-term monitoring of iron in the field.

In 2015, an autonomous spectrophotometric analyzer capable of providing vertical profiles as well as routine *in situ* determination of dissolved Fe(II) and Mn in seawater was proposed by Milani et al. [109]. The determination of Fe(II) was based on the red purple complex formed by Fe(II) and ferrozine which gave a maximum absorbance at 562 nm. This autonomous spectrophotometric analyzer contained microfluidic chip, pump, valves and electronic components which were fitted into a 15 cm diameter × 32 cm long cylindrical tube of anodized aluminum. The core of the analyzer was a colorimetric microfluidic chip (Lab-on-a-chip technology) which was manufactured in 8.0 mm thick tinted poly methyl methacrylate (PMMA). Samples and reagents were injected, mixed and the absorbance of the resulting complexes was measured by microfluidic chip. The analyzer was attached to the CTD frame on a custom made CTD -carousel [110] which had 9 Niskin bottles. Bottles on the rosette were Teflon coated and were used for water sampling at depth. The data system can directly communicate with Fe/Mn analyzer in real time *via* a RS232 port to initiate the measurement at a certain depth. Fe(II) and Mn could be measured with a frequency of up to 12 samples and 6 samples per hour, respectively. The detection limit for Fe(II) and Mn was 27 nmol L^{-1} and 28 nmol L^{-1}, respectively. This device showed the advantages of relatively low cost, low power usage, minimal reagent consumption, portability, tolerance to pressure up to at least 170 bars, high precision and high accuracy.

In situ sensors have great potentials for quantifying the spatial and temporal distribution of iron and its species in seawater, which is of great significance in studying iron marine biogeochemistry and the relationship between iron bioavailability and global carbon cycle. Further development is still needed to improve sensor reliability and data accuracy for long-term operation.

6. Conclusions and future perspective

The role of iron in the study of the marine biogeochemistry is significant due to the close relationship between iron and phytoplankton in seawater. The determination of iron in water samples, especially in seawater, seems to be perfect example of the connection and positive feedback between laboratory research works and real environmental need, as well as the improvement and evolution of analytical chemistry and marine chemistry. This paper reviews the various analytical methods for determination of iron in seawater from laboratory to *in situ* measurement based on the sensing strategies of atomic spectrometry, spectrophotometry, chemiluminescence, and voltammetry, *etc*. Although the excellent performance of determination of iron has been obtained and reported by most of research works in laboratory, it is still necessary to develop accurate analytical methods for determination of iron and its speciation, especially realizing *in situ* measurement. There is a high demand for the development of new measurement technologies with sensitive and fast detection, minimal sample treatment, or that can be used directly. It is better to carry out *in situ* determination of trace iron and its species. The VIP system mentioned above can be used for long-term monitoring and the autonomous spectrophotometric analyzer has advantages of low cost, low maintenance. The aforementioned techniques clearly show that there is a huge potential for realizing *in situ* measurements of iron in seawater. Further development is still needed to carry out reliable and long-term operations, because long-

term stability, fouling by organic matters/biofouling and sample treatment are the challenges that need to be overcome.

There is an urgent demand for new sensing methods and *in situ* measurement devices that can be operated remotely with wireless technologies for real-time iron and iron speciation analysis, and there are promising signs for future development of more reliable and long-term *in situ* iron sensing platforms, as such information is critical to the study of marine biogeochemistry and global carbon cycle.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2018.05.071.

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